



*Resonant
Inelastic
X-ray
Scattering
of soft x-rays*

*Resolving the crystal field excitations
in strongly correlated systems*



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Summary

RIXS of soft x-rays: Resolving the crystal field excitations in strongly correlated systems

INTRODUCTION TO THE TECHNIQUE

- RIXS and electronic excitations in $3d$ systems
- Instrumentation: going towards high resolution

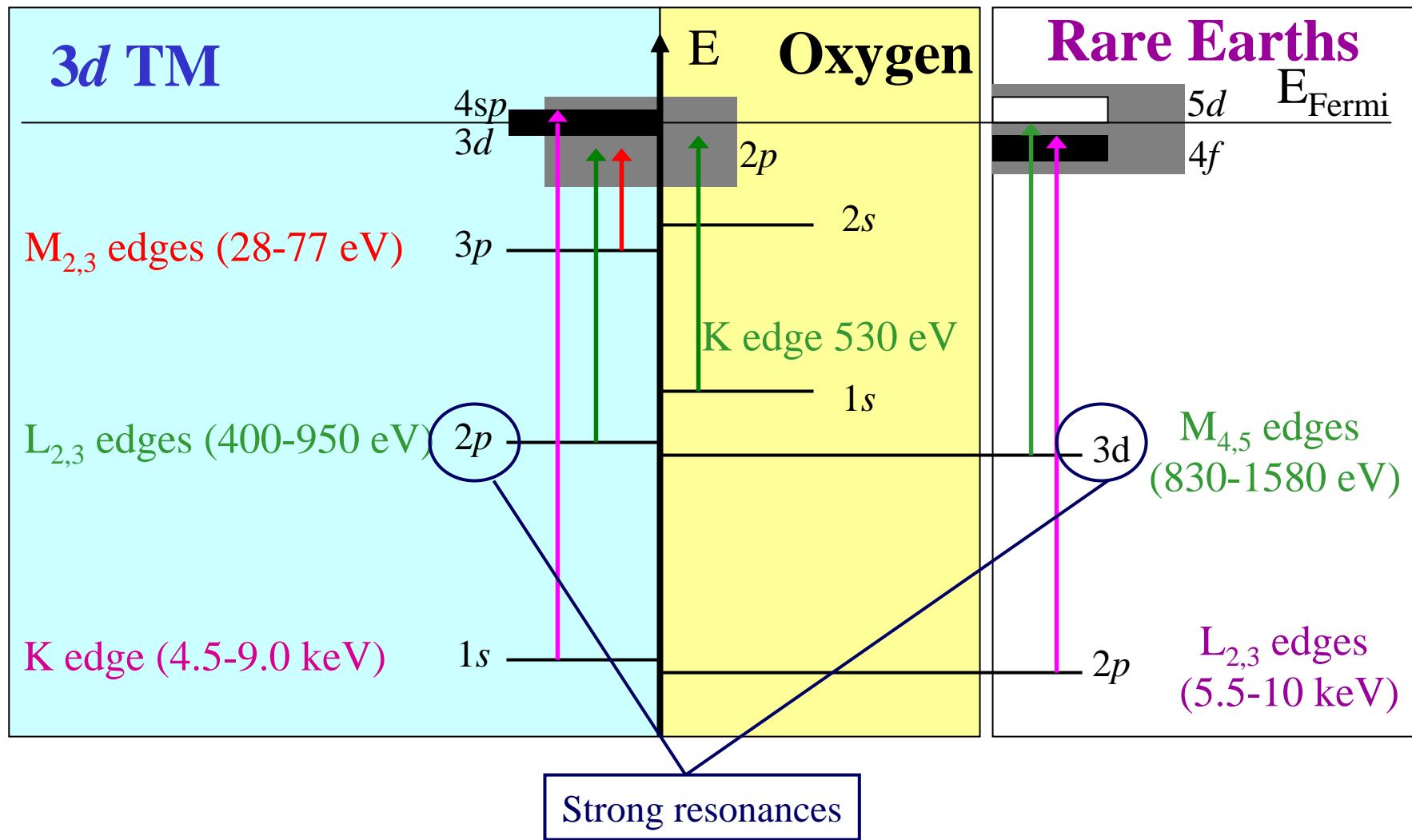
SELECTED EXAMPLES

- NiO: a prototypical case
- LaTiO₃ and YTiO₃: in search for the “orbitons”
- Manganites: dd excitations vs charge transfer excitations
- Cuprates: dd excitations, looking for the z^2 excitation

RIXS at the $2p$ and $3p$ resonances of $3d$ transition metals

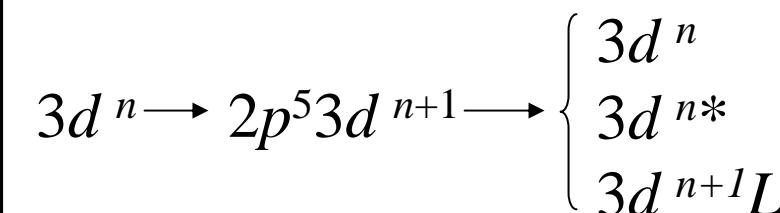
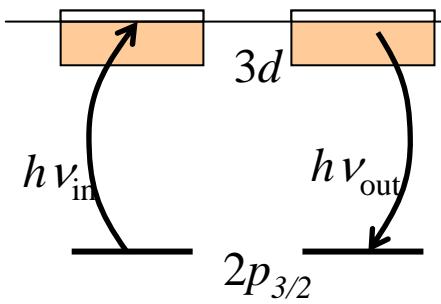
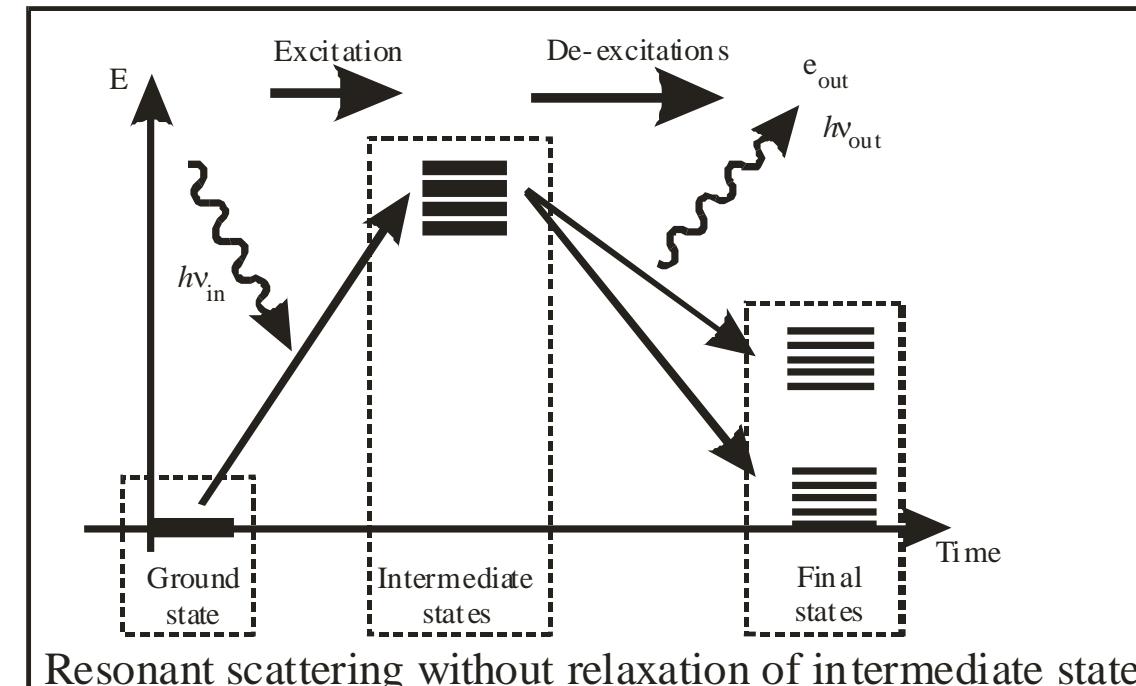
VUV energy range: 20 to 100 eV (62 to 12 nm)

Soft x-ray energy range: 50 to 1500 eV (25 to 8 nm)



L and M edge RIXS of 3d transition metals

L_3 RIXS: total energy representation



elastic peak
 dd excitations
 Charge Transfer

CuO: $3d^9 \rightarrow 2p^5 3d^{10} \rightarrow [3d^9; 3d^{9*}; 3d^{10} \underline{L}]$

NiO: $3d^8 \rightarrow 2p^5 3d^9 \rightarrow [3d^8; 3d^{8*}; 3d^9 \underline{L}]$

LaTiO₃: $3d^1 \rightarrow 2p^5 3d^2 \rightarrow [3d^1; 3d^{1*}; 3d^2 \underline{L}]$

L and M edge RIXS of 3d transition metals

M_{2,3} and L_{2,3} RIXS: final states

**NEUTRAL
EXCITATIONS!**

$\left\{ \begin{array}{l} 3d^n \\ 3d^{n*} \\ 3d^{n+1}L \end{array} \right.$

elastic peak: 0 eV

dd excitations: 0.xxx to 5 eV

Charge Transfer excitations: 2 to 10 eV

“Low” energy, neutral electronic excitations;
No core holes, no electron beams

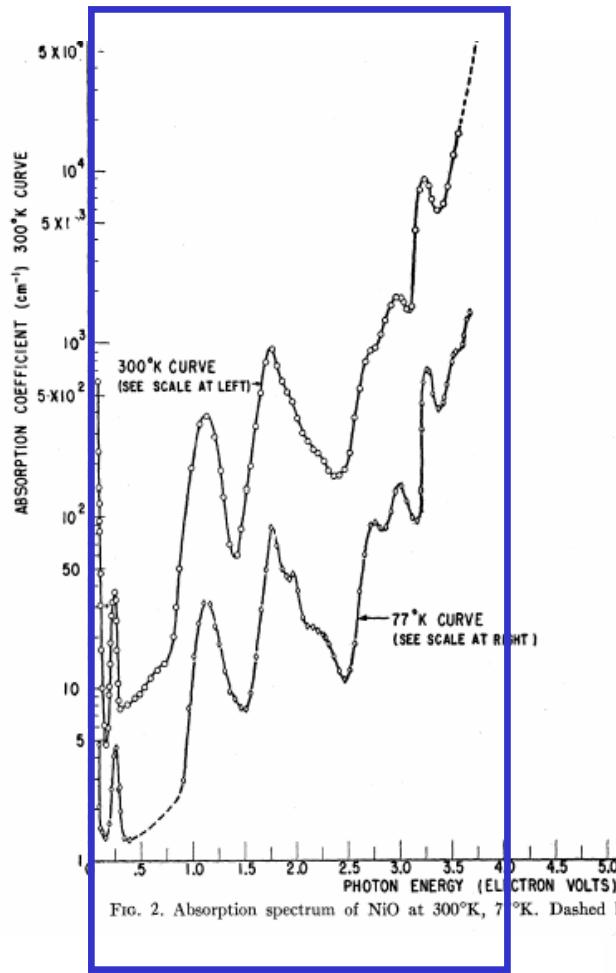
RIXS at M and L edges have the
SAME final states reached
via DIFFERENT intermediate states

M and L edge RIXS have the
SAME final states of EELS and Optical Absorption
but reached via E1 allowed radiative transitions
and SELECTIVELY on the chemical species

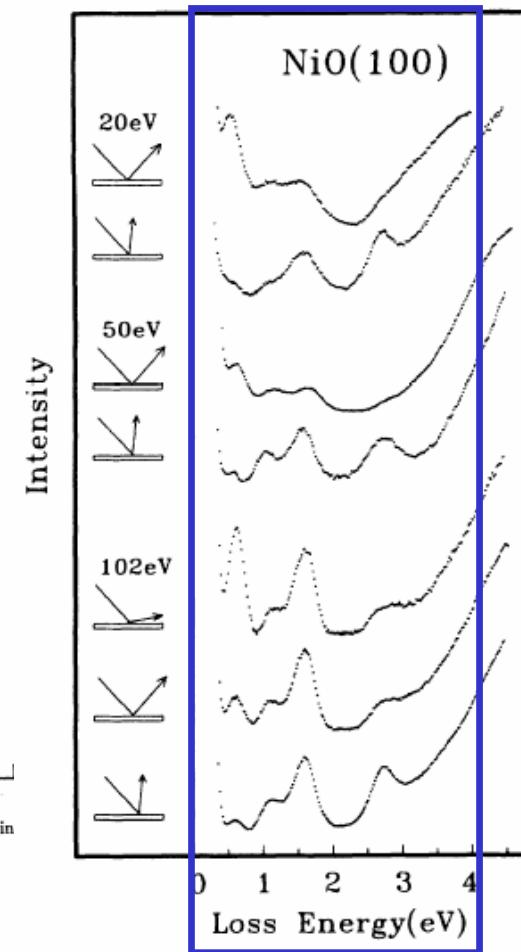
L and M edge RIXS of 3d transition metals

Other techniques can explore the same excitations

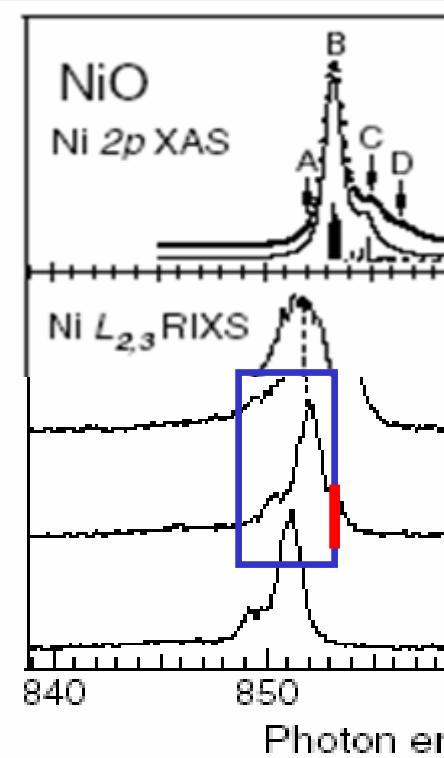
Optical Absorption



EELS (Electron Energy Loss Spectroscopy)



L_3 RIXS



NiO: $3d^8 \rightarrow [3d^8; 3d^{8*}]$

How many final states can we resolve?

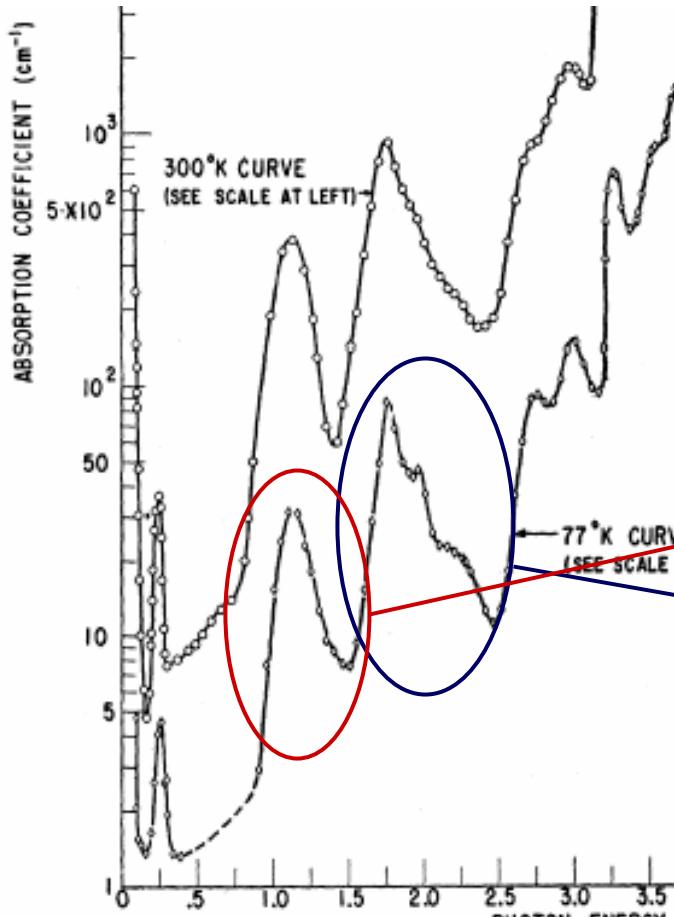
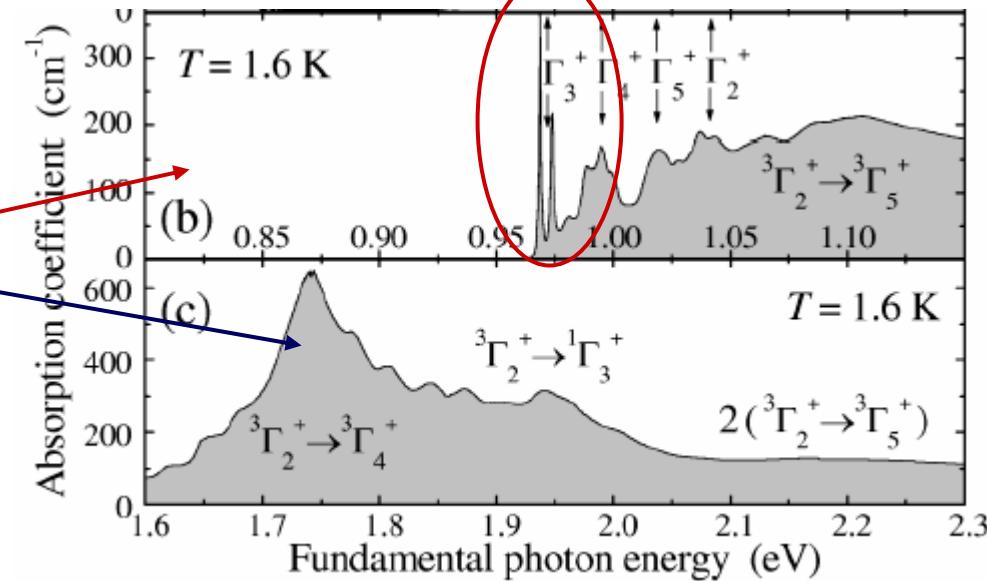


FIG. 2. Absorption spectrum of NiO at 300°K

Optical Absorption

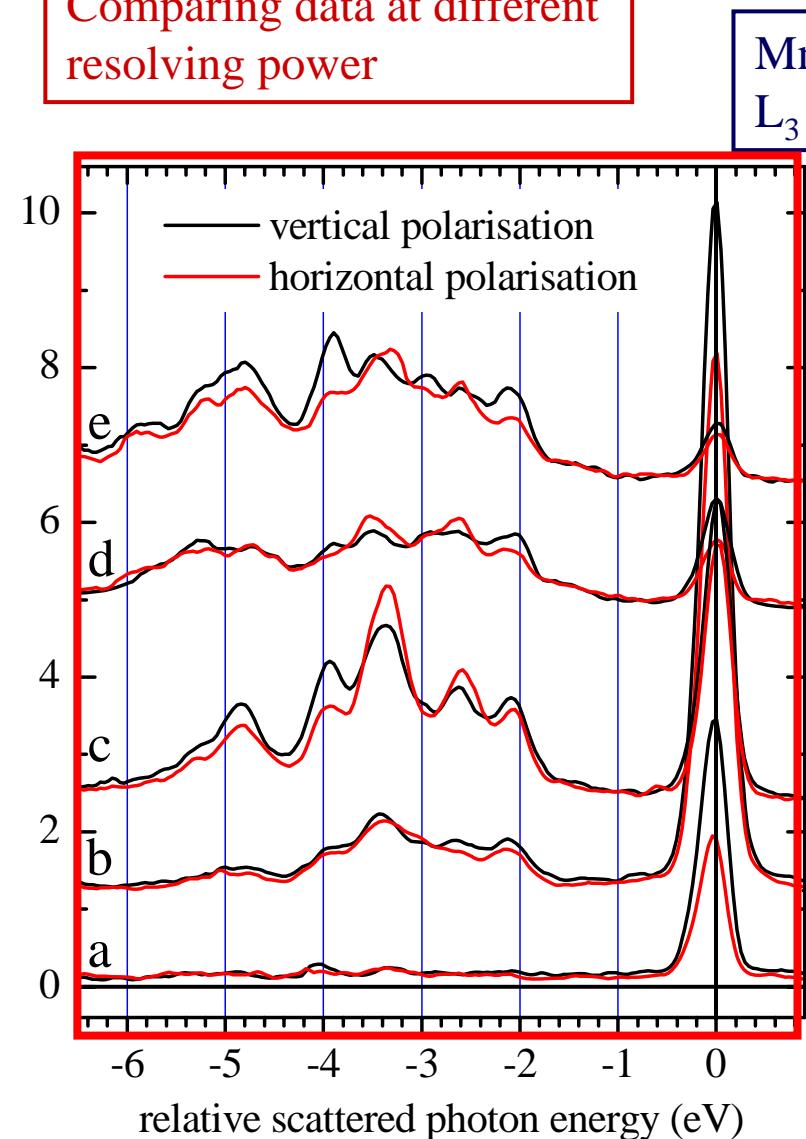
Peaks separated by less than 10 meV



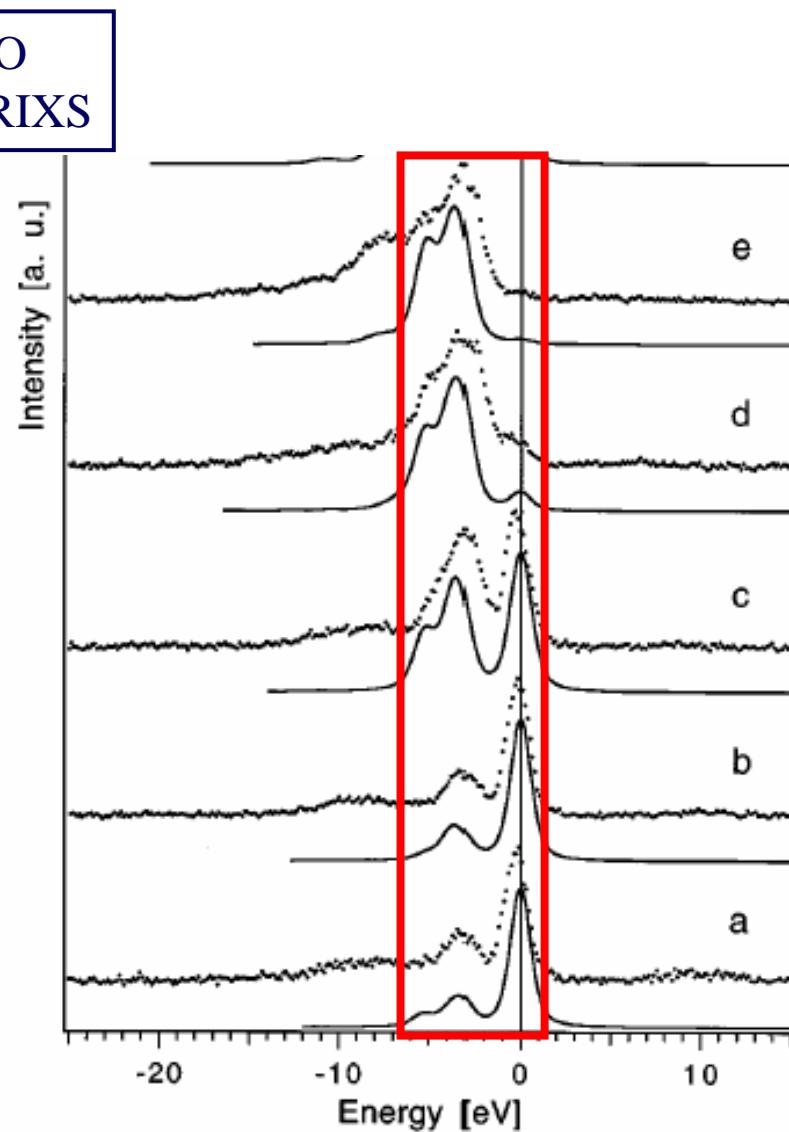
How far can we go with RIXS?

How many final states can we resolve?

Comparing data at different resolving power



G. Ghiringhelli *et al.* submitted to PRB
BW = 0.32 eV



S. M. Butorin *et al.* Phys. Rev. B **54**, 4405 (1996)
BW > 1.5 eV, Data and atomic calculations

How many final states can we resolve with RIXS?

COMBINED RESOLUTION

Energy resolution for $h\nu_{\text{in}}$: to choose the intermediate state

Energy resolution for $h\nu_{\text{in}}$ and $h\nu_{\text{out}}$: to separate final states

ΔE_{in} and ΔE_{out} should be the same (ideally)



The spectrometer should be as performing as a GOOD monochromator

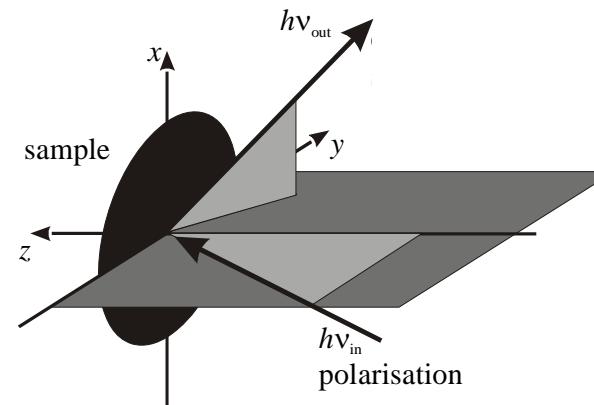
EXAMPLE

100 meV combined energy resolution for 1 eV excitation:

$E/\Delta E = 10$ in optical absorption

$E/\Delta E > 300$ at M edges

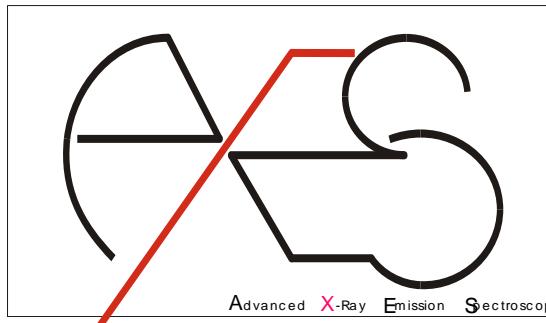
$E/\Delta E > 4000$ at L edges



Instrumentation for soft x-ray RIXS

OUR spectrometer

AXES at beam line ID08 of the [ESRF](#)
using a dedicated monochromator



Sample

Entrance slit
(20-60 μm)

$\sim 600 \text{ mm}$

$\sim 1600 \text{ mm}$

Position sensitive
detector (pixel = 13.5 μm)

1993: Designed and built by
Lucio Braicovich

Optical scheme: VLS spherical grating

Grating: 2400 l/mm

entrance slit

Detector: CCD at normal incidence

Energy range : 500 to 1500 eV

$E/\Delta E = 2000$ at Mn L₃ edge (640 eV)

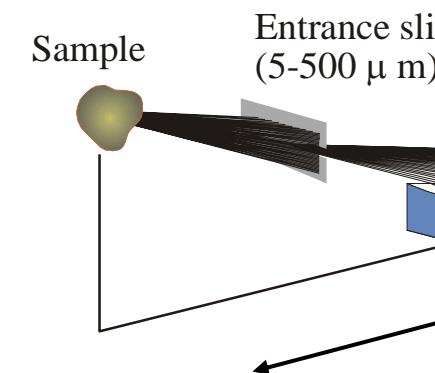
$\Phi_{\text{MAX}} = 0.6^\circ \times 0.4^\circ = 0.7 \times 10^{-4} \text{ srad}$



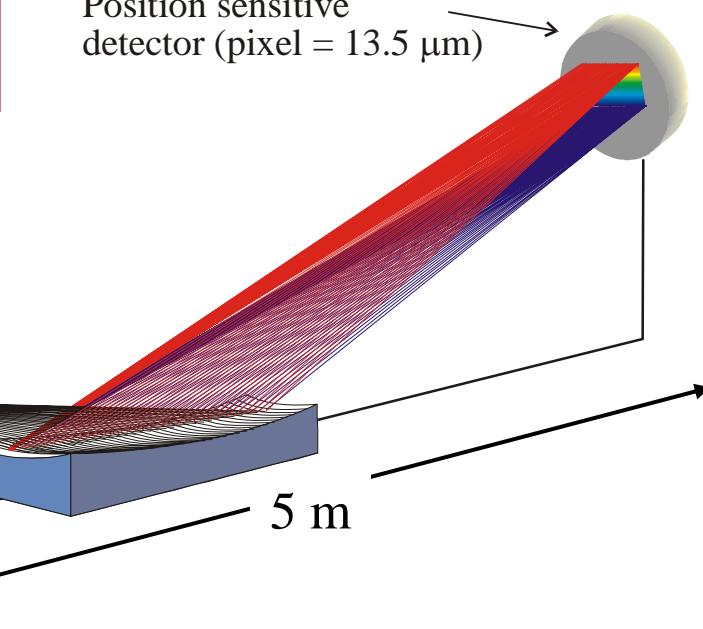
AXES is property of the CNR/INFM
but it is open to external users through
the standard ESRF beam time
allocation procedure

Instrumentation for soft x-ray RIXS

Going to higher resolving power:
the SAXES project at beam line ADDRESS of SLS



Position sensitive
detector (pixel = 13.5 μm)



Optical scheme: VLS spherical grating

Grating: 3200 l/mm

entrance slit (to be used for setting up only)

Detector: CCD at glancing incidence

Energy range : 400 to 1600 eV

$E/\Delta E > 10000$ over whole range (design target)

$\Phi_{MAX} = 0.3^\circ \times 0.25^\circ = 0.25 \times 10^{-4}$ srad

variable scattering angle (for k dependent RIXS)

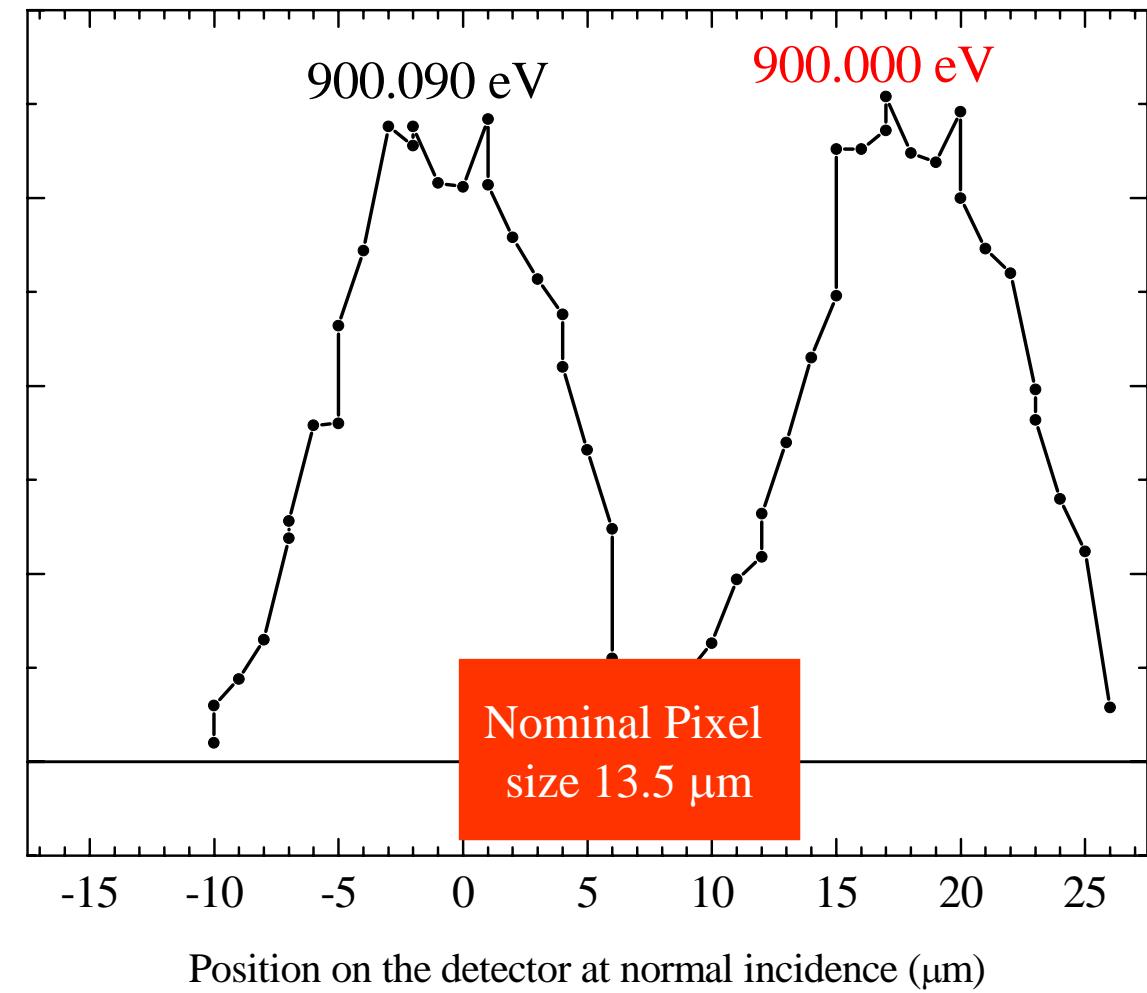


under construction

*operational from
autumn 2006*

Instrumentation for soft x-ray RIXS

SAXES: Ray tracing and the real pixel size

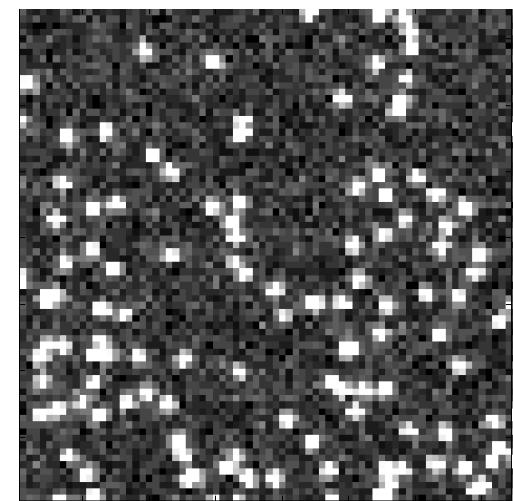
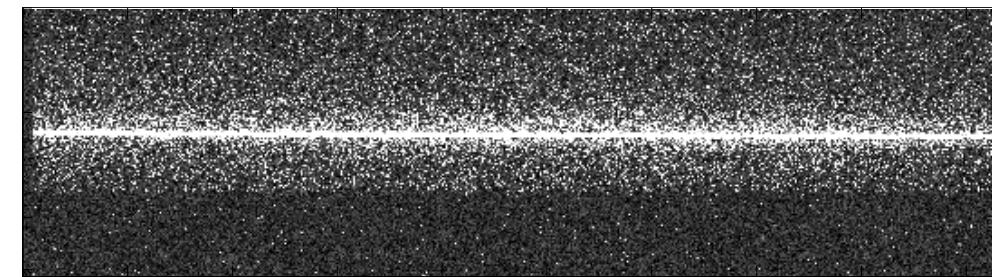
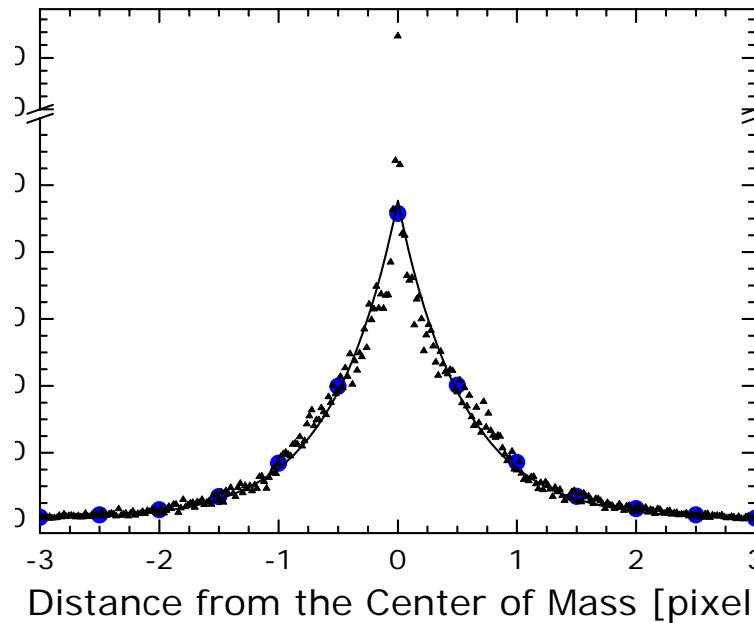


WARNING: the effective size of the charge cloud in CCD detectors is 25-30 mm,
irrespective of the pixel size!

Instrumentation for soft x-ray RIXS



SAXES: considering the real pixel size in CCD detectors



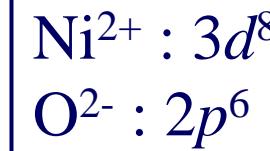
WARNING: the effective size of the charge cloud in CCD detectors is 25-30 mm, irrespective of the pixel size!

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- YTiO₃: in search for the “orbitons”
- Manganites: *dd* excitations *vs* charge transfer excitations
- Cuprates: *dd* excitations, looking for the z^2 excitation

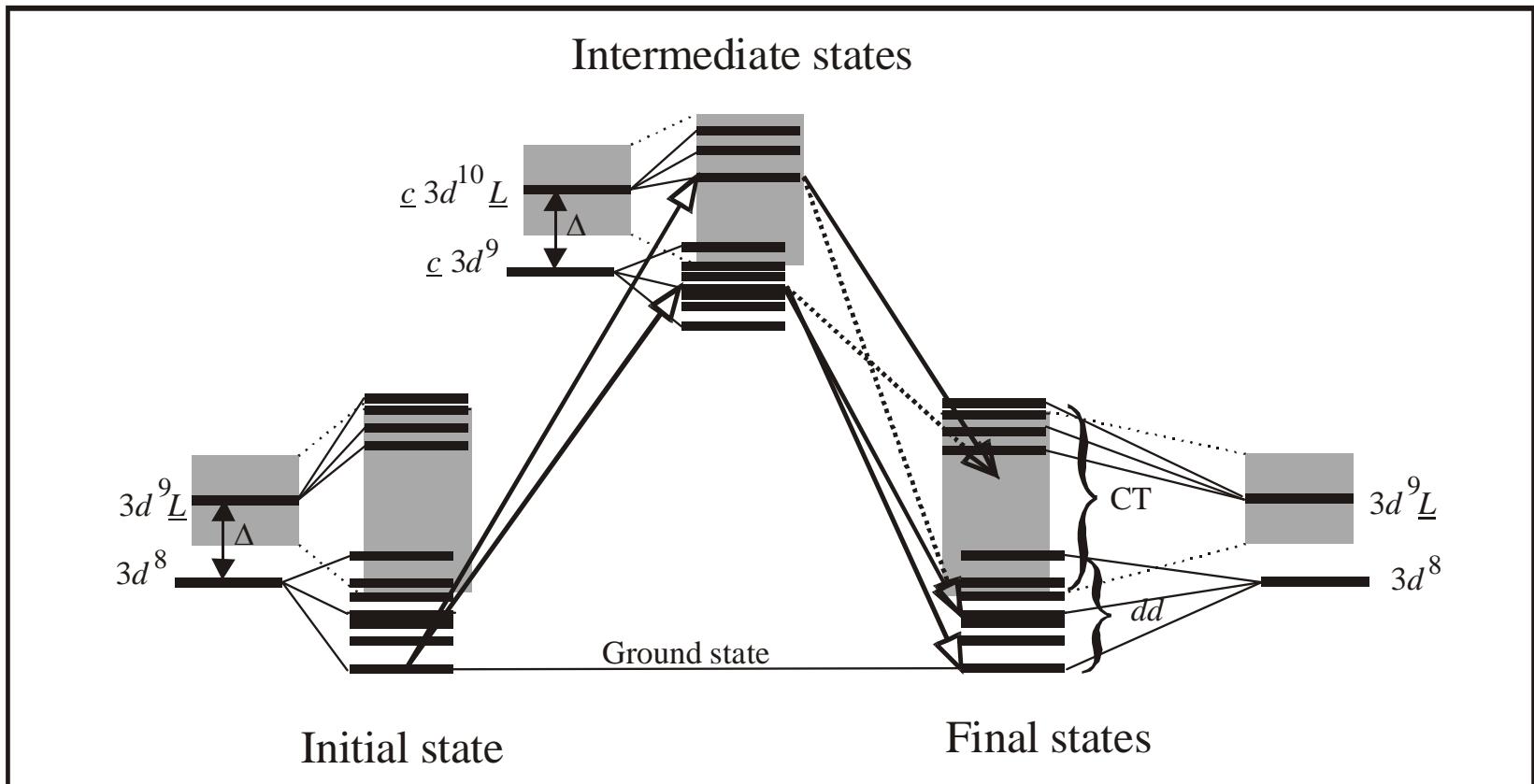
Recent data taken with AXES on 3d TM oxides
Combined resolving power better than 1500.

$M_{2,3}$ and L_3 RIXS of NiO

NiO: two holes
in the ground state

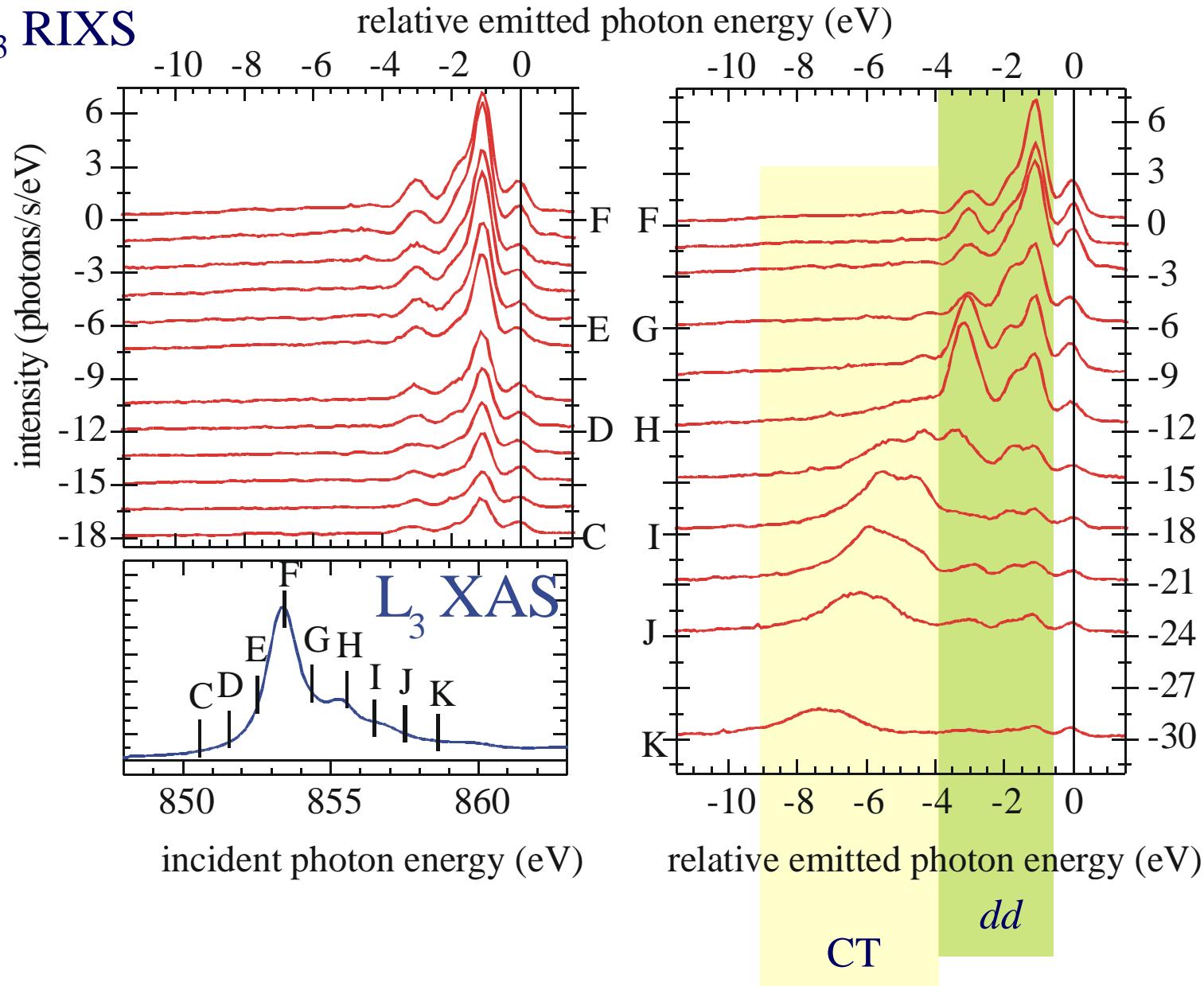


Single Impurity Anderson Model: configuration interaction



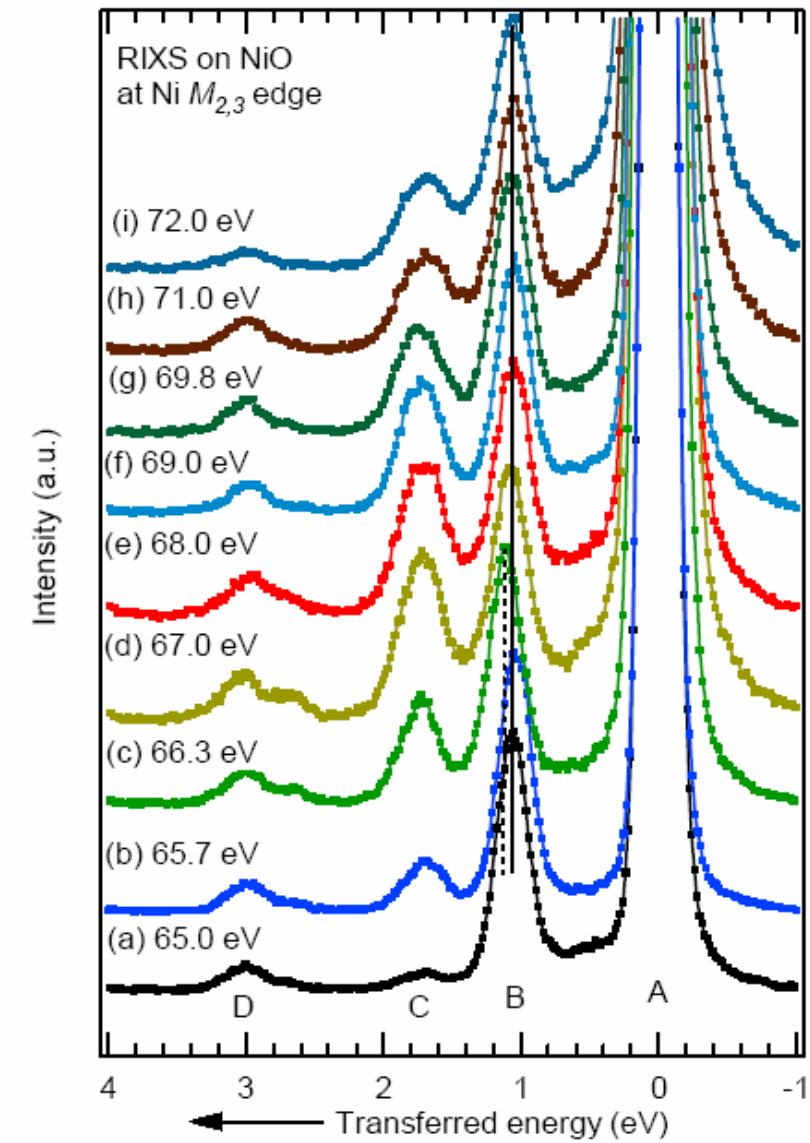
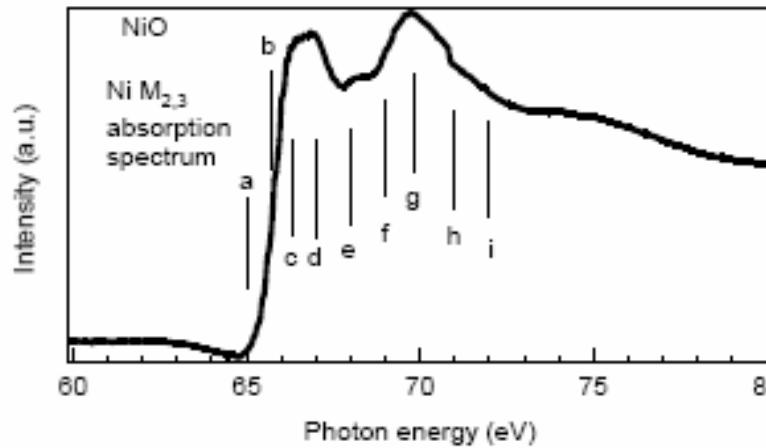
$M_{2,3}$ and L_3 RIXS of NiO

L_3 RIXS



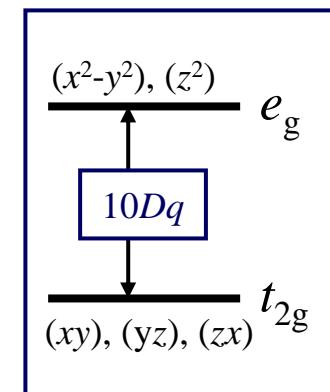
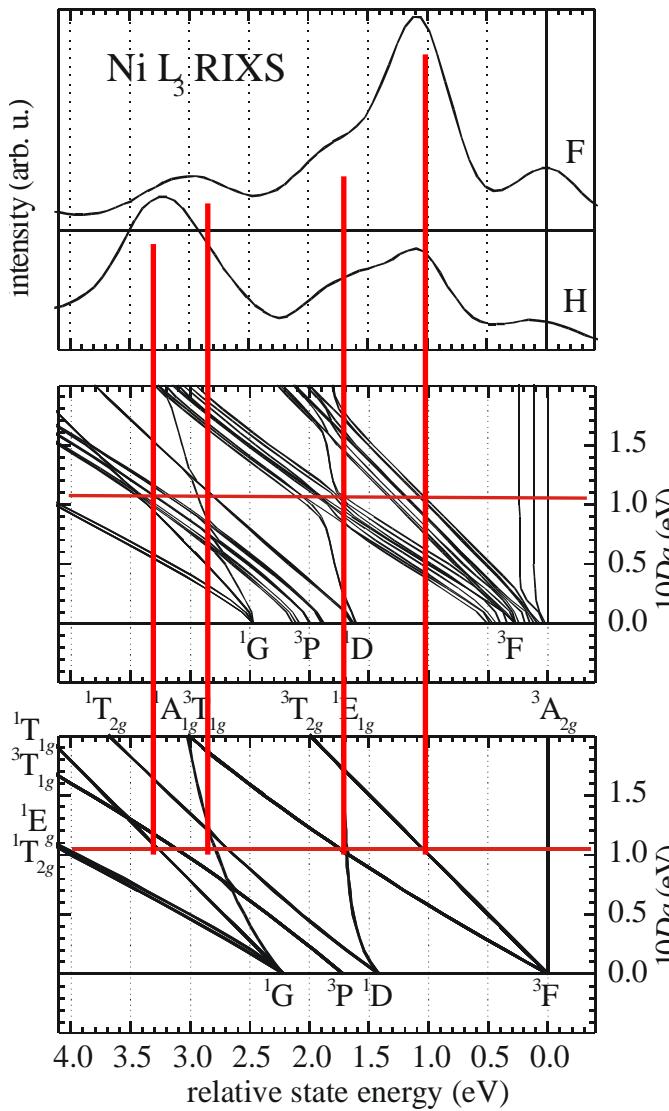
$M_{2,3}$ and L_3 RIXS of NiO

$M_{2,3}$ RIXS



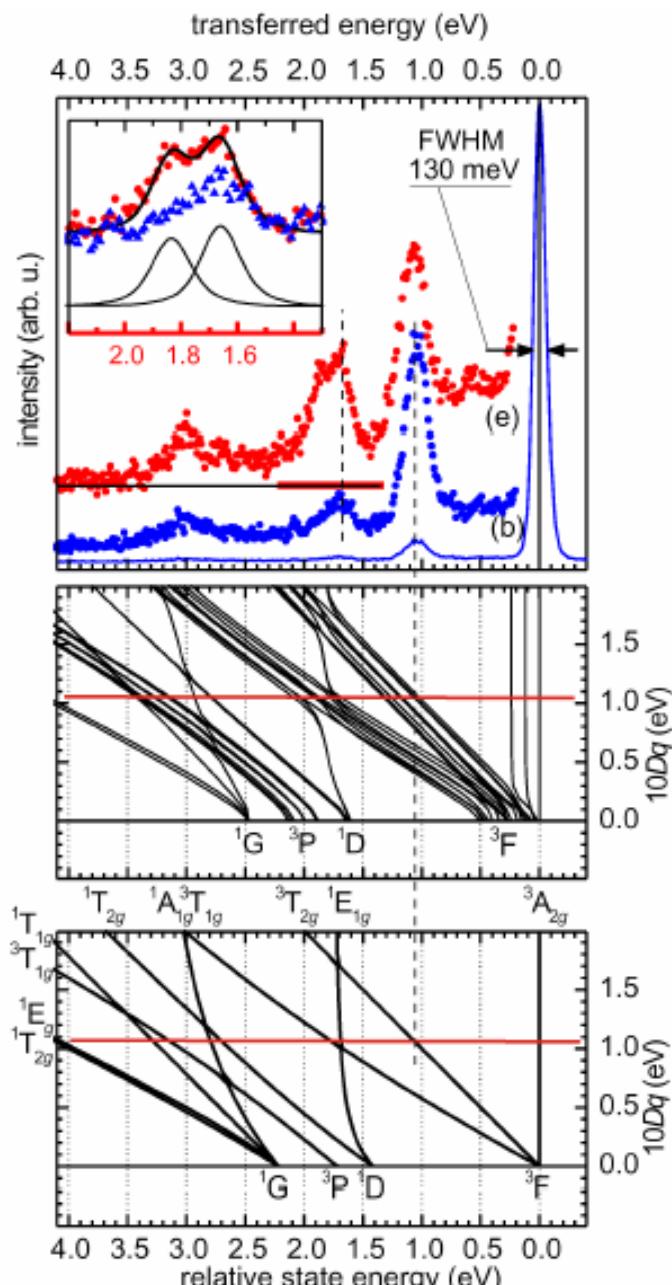
$M_{2,3}$ and L_3 RIXS of NiO

Crystal field model: Sugano-Tanabe diagram



Single ion
Octahedral C.F.
 $3d$ spin-orbit
Exchange

Single ion
Octahedral C.F.



L_3 RIXS of NiO

Crystal field model: calculated spectra

single ion, cubic crystal field

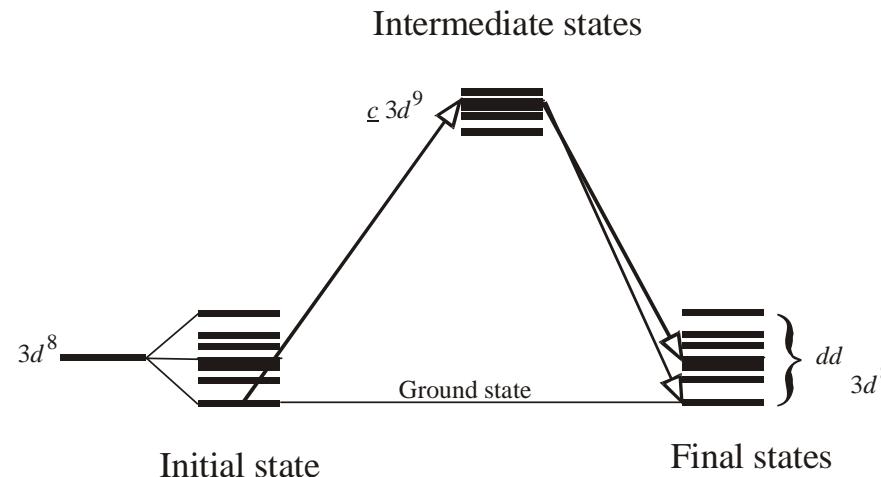
+

3d spin orbit and exchange interactions

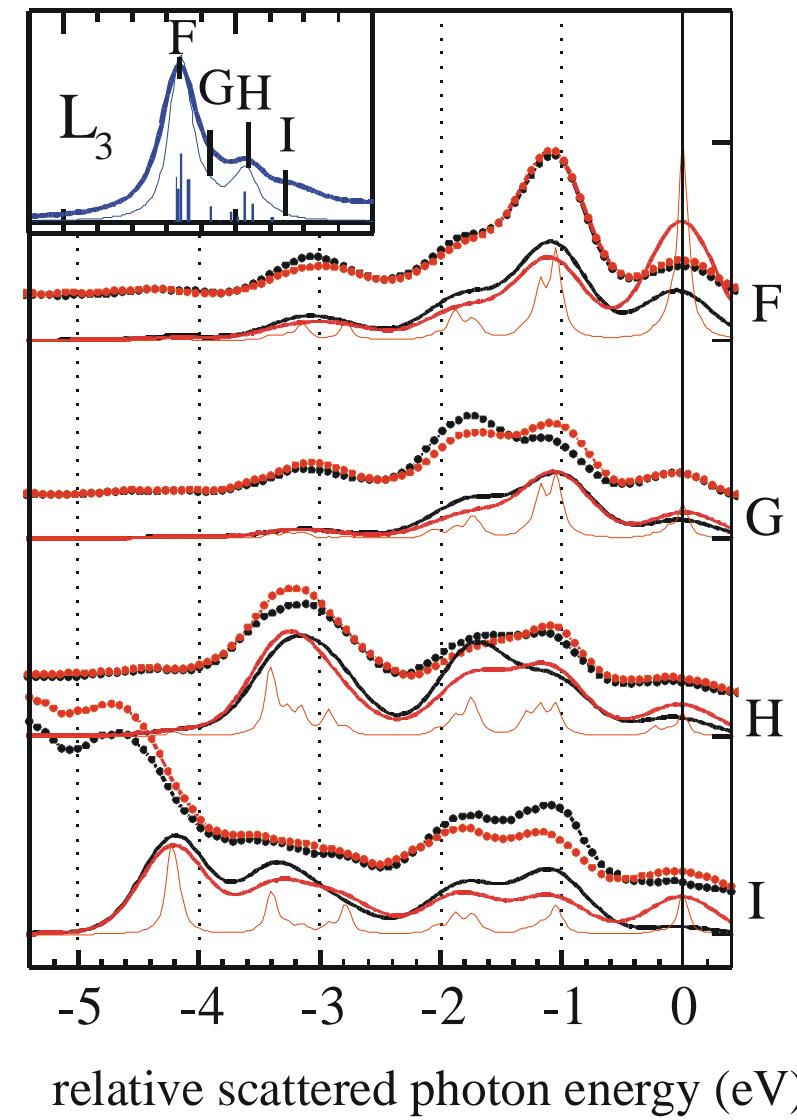
$$10Dq = 1.05 \text{ eV}$$

Slater Integral reduction 70%

Exchange interaction 120 meV

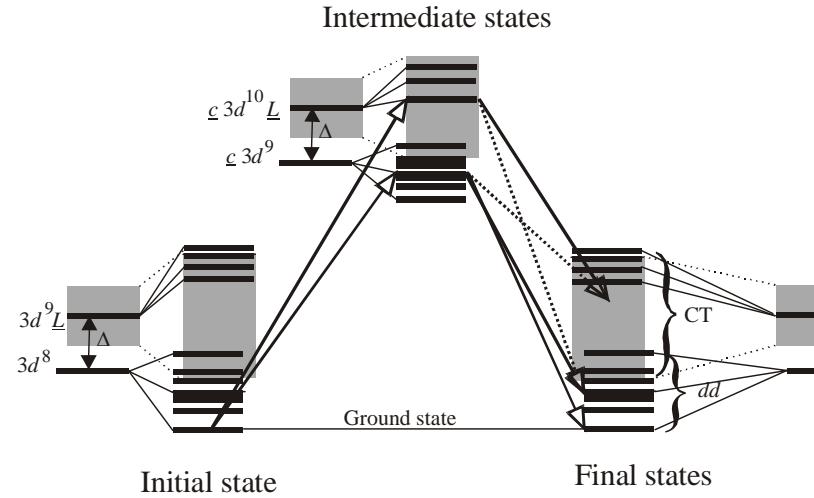


incident photon energy (eV)
 850 855



L_3 RIXS of NiO

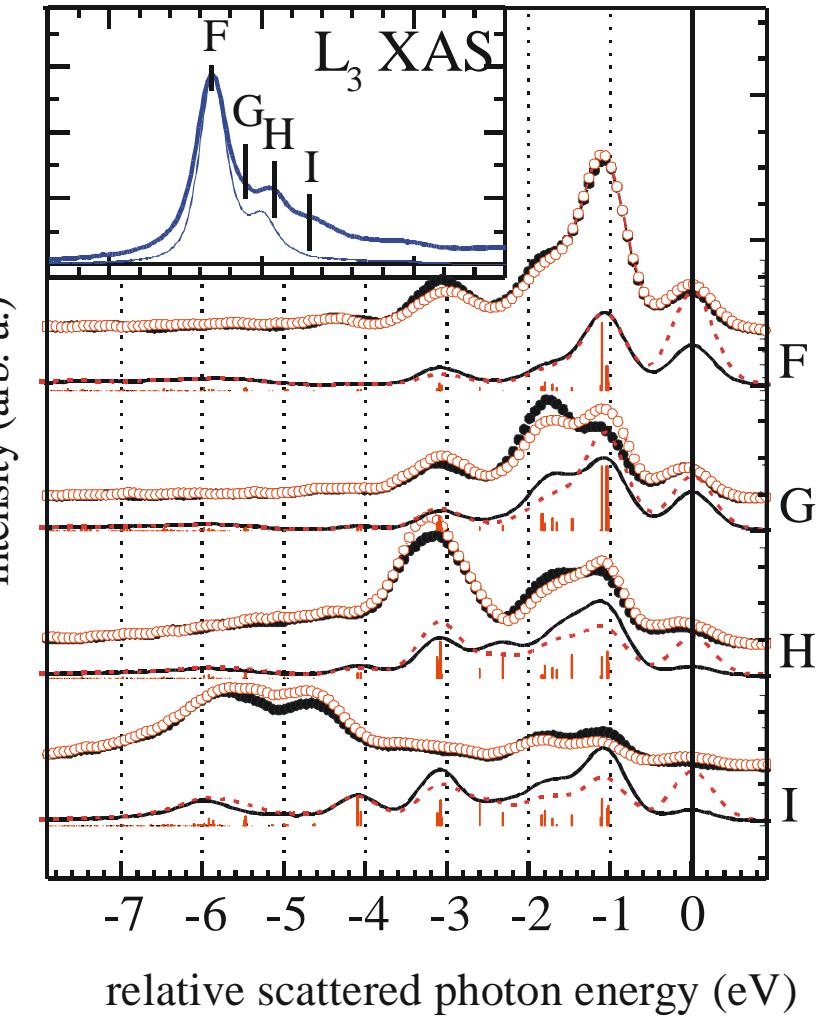
Impurity model calculations:
 CT excitations are included



Parameter	Value
$10Dq$	0.5 eV
Δ	3.5 eV
U_{dd}	7.2 eV
U_{dc}	8.0 eV
$V(e_g)$	2.2 eV
$V(t_{2g})$	-1.1 eV
W	3.0 eV
R_c	85%
$1/R_v$	0.8
	1/0.9

incident photon energy (eV)

850 855 860



1) The FRONTIER is to become a HIGH RESOLUTION SPECTROSCOPY

- energy resolution is difficult to obtain because we need high $E/\Delta E$
- the signal is very weak (due to cross sections and spectrometers)
- resolution has entered the 100 meV scale

2) The CURRENT development:

- it requires state of the art synchrotron beam line as a source
- calculations are relatively easy because the process is E1 allowed
- it probes hybridisation to the ligands and not only local effects
- it can be directly compared with other techniques (O.A., EELS)
- it is not surface sensitive because it involves no electron beams
- it can be performed in the presence of magnetic and electric fields
- it can be performed on insulators and metals
- it can be performed on thin films (less than 10 nm thick)
- it can be performed at low and high temperatures

3) The PERSPECTIVE is to get access to other excitations, such as

- magnons
- orbitons

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di Milano
&
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Source*

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